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THERMOELECTRIC COMPONENT

The present invention relates to a thermoelectric component, especially a thermocouple, according to the species defined in the main claim.

Background Information

In using thermocouples for measuring temperatures, one frequently runs into limits of material load capacity with regard to temperature and application atmosphere. Thus at present, in using thermocouples for a temperature range up to 1500° C based on PtRh/Pt elements, in extended use above 1000° C, there frequently appears a drift in the thermoelectric voltage, and simultaneously, a considerable deterioration of the mechanical properties on account of creep processes. In particular, during contact with carbon in such thermocouples, often metal carbides will form, which change the Seebeck coefficient and the mechanical properties of the thermocouple. In addition, PtRh/Pt thermocouples are very expensive to produce, and therefore not usable in certain applications.

It was the object of the present invention to make available a thermoelectric component that can be applied especially as a thermocouple, and which permits always making a precise temperature measurement even in ranges of durably high temperatures and/or transient temperature loads, as well as in oxidizing and also reducing gas atmospheres.

Summary of the Invention

The thermoelectric component according to the present invention has the advantage over the related art that it has a very good service life and very good constancy in the thermoelectric voltage that occurs, even at high temperatures and reactive gas atmospheres, a typical service life being

considered to be five years. In particular, the thermoelectric component according to the present invention, when used as a thermocouple, permits making temperature measurements of up to 1300° C as well as in an oxidizing and also in a reducing atmosphere, at a precision of less than ± 10° C. It is also advantageous that the thermoelectric component has a short response time to temperature changes, which is typically less than one second.

Besides that, the thermoelectric component according to the present invention can be constructed in a small size, so that with it, microstructured thermocouples or microstructured thermoelectric components can be made. Here, a microstructured component is understood to mean a component whose element has typical dimensions in the micrometer range.

Because of its good temperature stability and resistance with respect to reactive gas atmospheres, in the thermoelectric component according to the present invention, one can furthermore do without a ceramic or metallic protective tube, so that its use as a thermocouple makes possible accurate and, at the same time, fast temperature measurement.

To sum up, the thermoelectric component according to the present invention has the advantage of a long service life expectation, even in reactive gas atmospheres, at simultaneously high temperature resolution and rapid response time. Beyond that, it can be manufactured cost-effectively and, particularly when used as a thermocouple, it has typical thermoelectric voltages in the mV range, which are easily measurable.

Advantageous further developments of the present invention are seen in the measures described in the dependent claims.

Thus, the thermoelectric component is not only suitable as a thermocouple, but by impressing an external current upon it in

a manner known per se, it can also be designed as a Peltier element, in order to make it into, for example, a thermoelectric heating element or cooling element.

The element of the thermoelectric component are advantageously made of a first ceramic material and a second ceramic material differing from the first, of which preferably at least one includes additionally one or more suitable filler materials. In this fashion, the occurring contact voltages are clearly increased, because of the Seebeck effect. Especially suitable as filler material, advantageously for one of the element is a filler material having at least approximately metallic conductivity, and on the other hand, for the other element, an electrically semiconductive or insulating filler material.

Finally, in realizing the first and/or the second element of the thermoelectric component, it is also advantageous if the ceramic material of at least one element has been obtained by pyrolysis of a polymeric precursor material or a polymeric precursor material provided with one or more filler materials. In this connection, by the selection of the polymeric precursor material, and by the type and proportion of the filler materials in this precursor material, in an especially simple way, the thermal coefficients of expansion of the elements of the thermoelectric component can be adapted to each other.

By the way, the thermoelectric component can also be realized in that, in at least one vicinity of the contact location, just one element is made of a ceramic material, while the second element is made of a known metal that can be soldered.

Brief Description of the Drawings

The present invention is explained in greater detail with the aid of the drawings and in the following description.

Figure 1 shows a thermoelectric component in the form of a thermocouple,

Figure 2 shows the graph of the contact voltage or the thermoelectric voltage near the contact location of the two elements of the thermocouple as a function of the temperature at the contact point.

Exemplary Embodiments

The exemplary embodiments further explained, first of all relate to polymeric precursor materials, provided with filler materials, which are convertible into ceramic materials by pyrolysis. Such precursor materials or filler materials, respectively, are known from EP 0 412 428 B1 or from DE 195 38 695 A1. It is also known from these that one can produce molded articles using pyrolysis, by the addition of filler materials to the polymeric precursor materials used. In this connection, the specific resistance of the ceramic molded articles obtained can be set both by the choice of the filler materials and by the choice of the polymeric precursor material.

As the polymeric precursor materials for the exemplary embodiments which are further explained, polymers are particularly suitable which are convertible by pyrolysis into ceramic materials based on Si-C compounds, Si-C-N compounds, Si-Ti-C-O compounds, Si-C-O compounds, Si-B-C-N compounds, Si-B-C-O compounds, B-C-N compounds, Si-Al-C-O compounds, Si-Al-N-C-O compounds or Si-C-O-N compounds.

As filler materials in these polymeric precursor materials or the ceramic materials obtained after pyrolysis, respectively, on the one hand filler materials are suitable which have at least approximately metallic conductivity such as $MoSi_2$, Cr_3C_2, TiC, WC, TiN, FeCr, FeCrNi, ZrN or ZrC. Besides those, or alternatively to them, an electrically semiconductive or

insulating filler material such as Al_2O_3, SiC, B_4C, BN, ZrO_2, SiO_2, Si_3N_4 or graphite also come into consideration as filler material.

As a low-ohm, high temperature-stable filler material having approximately metallic conductivity, especially molybdenum disilicide having a specific electrical resistance of $2x10^{-5}$ Ωcm and a positive temperature coefficient of the electrical resistance of $5x10^{-3}$ K^{-1} is particularly suitable.

As a high-ohm insulating, high temperature stable filler material, Al_2O_3 is preferably used, having a specific electrical resistance of more than 10^{11} Ωcm at room temperature, which is combined with a ceramic material based on an Si-O-C compound as conductivity carrying phase, whose specific electrical resistance after pyrolysis at 1400° C is about 2 Ωcm.

A first exemplary embodiment of the present invention is explained with the aid of Figure 1. Figure 1 shows a thermoelectric component in the form of a thermocouple 5, which has a first element 10 and a second element 11 which are connected to each other by a contact point 12 in the form of a thermal contact. It is further provided that thermocouple 5 is interconnected with a device for measuring the contact voltage. Thermocouple 5 is used for measuring a temperature to which contact point 12 is exposed. This temperature typically lies in the range of 0° C to 1500° C.

Figure 2 shows the plot of thermoelectric voltage which occurs in the vicinity of contact point 12 of thermocouple 5, as a function of the temperature to which contact point 12 is exposed. One can see from Figure 2 that the thermoelectric voltage that appears, lies in the mV range, and that, in the range of ca. 50° C to 1000° C, it is a linear function of the temperature.

In the exemplary embodiment explained, thermocouple 5 in its two elements 10, 11 further includes a single pyrolysis ceramic filled, however, with two different filler materials, whose electrical properties with regard to the Seebeck coefficient and the specific electrical resistance of first element 10 and second element 11 have each been set specifically by the type of the filler material.

The shaping of thermocouple 5 before the pyrolysis here was done using familiar manufacturing processes of plastic methodology, such as transfer molding, injection molding or hot pressing.

Especially important for the functioning of thermocouple 5 is the vicinity of contact point 12 in which the two materials of first element 10 and second element 11 meet each other. In this contact area, in which the thermoelectric voltage appears, it is important that the two materials of the first and the second element 10, 11 each be as homogeneous as possible in the vicinity of contact point 12.

During pyrolysis of the first used polymeric precursor materials, which form elements 10, 11, in order to avoid having different shrinkages in first element 10 or second element 11 occur, which can lead, particularly in the area of contact point 12, to cracks and thereby malfunctioning of the thermoelectric component, it is further provided, in a preferred specific embodiment, that the materials employed before the pyrolysis be adapted to one another with respect to the shrinkage appearing during pyrolysis. This adaptation is preferably made by the selection of the filler materials and their proportion in each polymeric precursor material.

In addition to the adaptation with respect to shrinkage, it is preferably provided further that the thermal coefficients of expansion of the material of the first element 10 and the material of the second element 11 be adapted to each other, so

as to minimize or avoid stresses and/or cracks in the area of contact point 12 during the operation of thermocouple 5.

Within the framework of the explained exemplary embodiment, the electromotive force or the Seebeck coefficient of the materials of first element 10 and of second element 11 is set only by the type of filler material used, whereas both elements 10, 11 are otherwise made of the same polymeric precursor material before the pyrolysis. Thus, for one of the elements 10, 11 of thermocouple 5, molybdenum silicide is used as high temperature-resistant filler material, having approximately metallic conductivity. In that case, electrically semiconductive or insulating filler materials, such as aluminum oxide or graphite can be used. In addition, however, it is also possible to make one of the two elements 10, 11 of thermocouple 5 completely of a metal that can be soldered, such as Vacon (manufacturer: VAC Vakuumschmelze) that is, a Ni-Co alloy having a low thermal coefficient of expansion. In that case, the second element of thermocouple 5 is then made of the ceramic material which is filled with one of the filler materials discussed.

An alternative exemplary embodiment of thermocouple 5 provides that, as materials for first element 10 or second element 11 two different polymeric precursor materials be used, which will be present after pyrolysis in the form of two different ceramic materials, such as a Si-Ti-C-O compound on the side of element 10 and a Si-C-O compound on the side of the other element 11.

In this case, contact point 12 is composed in the form of a thermal contact having a thermal voltage appearing for a thermocouple 5 from adjacent pyrolytic ceramics of different composition, preferably having different filler materials.

It should be emphasized, by the way, that, besides the kind of filler material, alternatively or additionally to the

preceding exemplary embodiments, the proportion of the filler material in the polymeric precursor material(s) used can also be varied, so as to set the thermoelectric and the mechanical properties in this fashion, especially the Seebeck coefficient in contact area 12 of the thermocouple 5 so obtained.

Here, the entire filler material content lies between 10% by volume and 50% by volume, in relation to the volume of the initial blank present before the pyrolysis, including the polymeric precursor materials discussed.

Finally, it should be mentioned that the thermal voltage or the Seebeck coefficient, appearing in the area of contact point 12, can also be set, within certain limits, by the method parameters during pyrolysis, in all the preceding exemplary embodiments.

Subsequently, an exemplary embodiment for producing a thermocouple 5 according to Figure 1 will now be explained in greater detail. Alternative exemplary embodiments can be realized without further consideration by one skilled in the art, having the knowledge of documents EP 0 412 028 B1 or DE 195 38 695 A1, by varying the type and the amount of the filler materials used, or of the polymeric precursor compounds used.

To begin with, 53.1 g pulverulent condensation-cross-linked polymethylsiloxane and 46.9 g Al_2O_3 powder are placed in a grinding mill per 1000 g of steel grinding balls. This corresponds to a filling ratio of 20 % by volume of Al_2O_3 with respect to the polymer filler material mixture. After a grinding time of 5 minutes, the powder mixture obtained is separated from the steel balls and screened using a 150 µm sieve. Subsequently, the screened powder mixture is filled into a mold and is cold-molded at a pressure of 150 MPa. The first powder mixture is thus used as a first polymeric precursor material furnished with a first filler material,

from which subsequently first element 10 of thermocouple 5 will be formed.

For second element 11 of thermocouple 5, likewise, to begin with, 35.3 g pulverulent, condensation-cross-linked polymethylsiloxane and 64.7 g molybdenum silicide are used per 1000 g of steel grinding balls. This corresponds to a filling ratio of 25 % by volume of molybdenum silicide with respect to the polymer filler material mixture. After grinding and screening, which is carried out as described above, the powder mixture is then filled, as second polymeric precursor material furnished with a second filler material, into the mold, in which there is already the material for first element 10. After a cold-mold procedure at 150 MPa, the material junction thus obtained is next age-hardened for 30 minutes at a pressure of 10 MPa and a temperature of 170° C.

Subsequently, U-shaped molded articles as in Figure 1 are separated out (of the mold), which are then pyrolyzed according to the following temperature program under a flowing argon atmosphere having an argon flow of 5 l/min. Thermocouple 5 obtained from this temperature program has a thermal voltage which is in the thermal voltage range of known thermocouples based on PtPh/Pt. The temperature dependence of the occurring thermal voltage of thermocouple 5 that is obtained is shown in Figure 2.

Heating Rate/ Cooling Rate (°C/h)	Final Temperature (°C)	Retention Time (hours)
300	300	0
20	900	0
80	1400	1
150	20	-

Thermocouple 5 as in Figure 1 has typical dimensions of width of elements 10, 11 of 10 µm to 1 cm and a thickness of

elements 10, 11 of 1 µm to 1 cm. Furthermore, the typical length of elements 10, 11 is in the range of 1 cm and more. The distance apart of the first and second element 10, 11 in the region of thermocouple 5, in which these two elements 10, 11 run parallel to each other, is between 50 µm and 5 cm. Thermocouple 5 can thus be made especially even as a microstructured thermocouple having typical dimensions in the micrometer range. Besides, it is clear that, instead of a thermocouple 5, a thermoelectric component in the form of a Peltier element can also be made in the manner explained above. Then too, more than one contact point 12 can be provided, which are made of relevant material combinations for elements 10, 11 that define these contact points 12.

It is further obvious that the geometry of thermocouple 5 is not limited to the U-shape explained in accordance with Figure 1, i.e. there are other geometries too, and other dimension of the thermoelectric component which can be realized, according to the response time desired.